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Control of Environment Assisted Cracking of Al 7075 Using Inhibitors

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PREFACE

This report is the second one published by the Chemistry Research Division concerning the effects of nitrates on the mechanical properties of Al 7075. The findings reported are the result of several programs conducted over a 5 year period.

This report highlights the program of the Chemistry Research Division, Materials, Fuels and Lubricants Directorate, to formulate an inhibitor for use against environmentally assisted crack growth in 7xxx series aluminum alloys. The object of this program was to develop an aqueous corrosion inhibitor system(s) that could minimize or inhibit environmentally assisted fatigue crack initiation, or retard crack propagation or growth in aluminum alloy structures, thereby minimizing the possibility of environmentally induced catastrophic fatigue failure. The work reported includes both mechanical and electrochemical testing of the aluminum alloys exposed to the inhibitor formulas. The program produced 6 candidate formulas for crack inhibition, and identified 12 formulations which have possible application as general corrosion inhibitors.

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SECTION I. BACKGROUND

In response to the Army's increased use of high strength aluminum alloys in ground support equipment, the Chemistry Research Division, Materials, Fuels and Lubricants Directorate, Belvoir Research, Development and Engineering Center, undertook the task of finding a corrosion fatigue inhibitor appropriate for both depot and field use. The need for a field applicable corrosion fatigue inhibitor rose with the increased requirement for rapid deployment-air mobile field support equipment. This requirement mandated the increased use of high strength aluminum alloys, due to their high strength-to-weight ratio. The 7xxx series aluminum alloys in particular have been found to be highly desirable engineering materials which combine a high strength-to-weight ratio with a very favorable weight-to-volume ratio. These properties were successfully used by the aircraft industry for a number of years. On the negative side, an alloy such as Al 7075-T6 is very susceptible to both stress corrosion cracking and corrosion fatigue, and therefore requires protection of some type.

(NOTE: At this time, stress corrosion cracking and corrosion fatigue are both referred to by the single phrase *environment assisted cracking* because, in most cases, we cannot distinguish between the two types of corrosion.)

In the aircraft industry, the 7xxx series alloys—which are widely used as structural support members and for which application these alloys were developed—are usually covered by alclad aluminum sheets or, if in sheet form, used as an alclad product depending on the heat treatment. In turn, these alclad sheets are generally painted. When the surface of any item is painted, the following facts need to be kept in mind:

- Every painted surface has holes or holidays.
- For the same environment, the corrosion attack occurring at a holiday is generally more severe than on a bare metal surface.
- Inhibited paints and primers are not effective in dealing with environmentally assisted cracking.^{1,2,3}

Another aspect is the temper or heat treatment of the aluminum alloy. Corrosion specialists regularly refer to Al 7075-T6, -T651, -T73, and -T7351 as if each one is a separate and distinct alloy; on the other hand, design engineers tend to refer to them as if there were no distinctions among them. While all the different tempers are chemically indistinguishable from each other, each possesses a set of mechanical and corrosion resistance properties unique to that heat treatment. The T6 treatment produces the highest strength material and also the greatest susceptibility to environment assisted cracking (EAC). The T73 treatment greatly reduces this susceptibility to EAC, but at the cost of sacrificing some of the material's strength.^{4,5,6}

For the reasons outlined above, both the US Air Force ^{7, 8, 9, 10} and the US Navy ^{11, 12, 13} established inhibitor programs directed at minimizing the environment-assisted cracking threat in their respective operating environments. Shortly after the start of this program, the Air Force published their results on the development of a rinse type inhibitor system, which was to be used after every flight.^{7, 8} The Navy work performed at the Naval Air Development Center aimed for a more persistent type of inhibitor formulation due to the sea conditions aboard aircraft carriers. The Air Force formulations did not appear to provide enough long term protection to be adopted for use with tactical field support equipment, especially if sporadically applied. There was also a question of possible ground or ground water contamination if applied in the field due to the apparent volume required. Because the Navy base formulation contained hexavalent chromium, it was automatically proscribed in two states and could not be used in the field in several other states due to the potential of ground water contamination if spilled or washed off. Other factors considered in evaluating both the Air Force and Navy inhibitors for Army use were that:

- On many air mobile items, the paint thickness are minimal due to weight considerations.
- Items in depot storage or forwardly deployed are not washed down or cleaned until deployed to the field.
- On fielded items, the paint surfaces are broken due to stones, collision impact, and the very act of deployment or redeployment.

It was therefore determined that neither system was sufficiently adequate to be adopted for Army use. Therefore, using the Air Force and Navy work as guidelines, we undertook development of our own formulation. The general properties of any environment-assisted cracking inhibitor are shown below and cover our two main areas of concern—first, to produce an environmentally "safe" product, and secondly, to produce a product without a negative effect on the general corrosion resistance of all the materials used. These general properties are:

- Non-toxic and non-irritating
- Not water soluble once applied
- Inhibits crack initiation
- Inhibits crack growth
- Inhibits the initiation of corrosion
- Deactivates the sites of active corrosion
- Works over pH range 3.5 - 10.0 (ideal pH = 2.0 - 12.0)
- Works over temperature range 40° - 125°F
- Works in every type of environment
- Waterborne

Any possible EAC inhibitor formulation has the potential to interact not only with the surrounding environment, but with the base alloy of interest and with all other metals present in a manner apparently contradictory to its EAC inhibiting role. It is possible for the very reaction which inhibits EAC type corrosion to enhance the general corrosion of any metal, just as it is possible for a good general corrosion inhibitor to induce EAC type corrosion behavior in an otherwise passive surface. Similarly, just because a formulation is effective for one series of aluminum alloys, it does not mean it will necessarily be as effective for any other series of aluminum. In working with any type of inhibitor formulation, the usual way of controlling the negative effects is to introduce another additive or additives which will counteract the undesired effects more than they lessen the positive effects.

The chemistry of the reacting system—except in what are known as closed, or closed-looped systems—cannot be controlled closely enough to produce the exact results desired since the reacting system being open is neither monitored nor controlled. In order to justify time and effort expended, the developed inhibitor should withstand the worst type of operating environment in which it will be used. Therefore, the purpose of this program was to develop an inhibitor system which minimizes EAC in 7xxx series aluminum alloys, and not to study the chemical systems and reactions involved.

For the purposes of brevity and clarity, the following definitions from ASTM G-15, *Standard Definitions of Terms Relating to Corrosion and Corrosion Testing*, are used to define the two aspects of environment assisted cracking:

- **Corrosion fatigue**—the process in which a metal fractures prematurely under conditions of simultaneous corrosion and repeated cyclic loading at lower stress levels or fewer cycles than would be required in the absence of the corrosive environment.
- **Stress-corrosion cracking**—a cracking process that requires the simultaneous action of a corrodent and sustained tensile stress. (This excludes corrosion-reduced sections which fail by fast fracture. It also excludes intercrystalline or transcrystalline corrosion which can disintegrate an alloy without either applied or residual stress.)

Two of the shorter and more readable presentations on corrosion fatigue are by J. Schijve¹⁴ and R.N. Parkins,¹⁵ while Sanders and Staley¹⁶ present an excellent review on the fatigue of high strength aluminum alloys. The article by M. O. Speidel¹⁷ on test techniques in stress corrosion cracking presents the most readily readable treatment on stress corrosion cracking found so far.

SECTION II. EXPERIMENTAL TESTING

The test program was set up and run in two separate work sections: the primary screening of the formulations was done in the *electrochemical* test section (Appendix A), and the *fatigue* test section (Appendix B). The program was designed to work in five successive phases:

- Phase I. Identification of an appropriate test solution
- Phase II. Establishment of a baseline data field using known formulations
- Phase III. Screening of original formulations
- Phase IV. Development of surviving formulations from Phase III
- Phase V. Full spectrum test of candidates from Phase IV

PHASE I

Rather than simply choose a test solution to use in the test program, we decided to have the test systems establish a worst-case condition for themselves. The source of possible candidates was drawn from the solutions used in the various ASTM test procedures, as well as simulations of existing real-world environments. We set the lower pH limit to 3.5, based on what we knew at the time concerning acid precipitation¹⁸ and in an attempt to avoid some of the problems experienced by the Navy.^{11, 12, 13} The parameters used were fatigue life, pitting potential, pitting time, uniform corrosion rate, and surface resistance (Rp ohms).

PHASE II

The baseline tests were needed to be able to accurately gauge the relative effectiveness of any inhibitor formulation. Our test systems and test solutions would not be the same as those in the works we were referencing; therefore, we had no real idea what response would be produced in our test system by an effective inhibitor, nor how to really judge its effectiveness by the responses produced. In order to establish the needed parameters, several commercial formulations, along with the Air Force and Navy formulas, were run. The commercial formulations were for general corrosion and not for specific use against environment assisted cracking.

PHASE III

As stated in Section I, it is possible to develop a good inhibitor for EAC which also accelerates the general corrosion of the base metal. The electrochemical test portion of this phase sought to eliminate those formulations having little or no general inhibitive properties.

The fatigue testing portion of Phase III sought to answer the question: Would the formulation increase the fatigue life of the coupon when exposed to a hostile environment? In the electrochemical testing, the formulation could draw from the bulk solution to replenish itself at the metal-solution interface. In the fatigue test—as with actual usage—all the inhibiting power resides in the surface film formed by the test formulation.

For this Phase (III) of the program, we compiled an ordered list of compounds and combinations to be tested. Besides the Air Force and Navy references, the prime informational sources used in preparing our original formulations were a three-part series on waterborne coatings,^{19, 20, 21} Matasa and Setzer,²² Partridge,²³ and Roebuck.^{24, 25, 26} Other articles contributing to the formulation efforts are cited in references ²⁷⁻⁵⁴, while others ⁵⁵⁻⁷⁸ provided the background on the chemistry and mechanics of the environment assisted cracking processes. It was thought that this phase of the program would yield four to eight raw formulas which improved the fatigue life. These formulations would be reduced to a core of two to four base formulas for use in Phase IV of the program. The program was not continued beyond this third phase. Some of the factors examined during the course of the screening process are listed below.

SCREENING PROCESS FACTORS

Substitution of Different Molybdate Compounds

Using Mixed Molybdate Compounds

Surface Preparation

Wetting Agents

Different Triazoles

Mixing Phase-transformed Materials and Non-transformed Materials

Combining Ethoxylated Compounds

The formulation process was one of individually substituting one compound for another, then adding or deleting an additive which had previously shown some positive effect. At the close of the program, the electrochemical testing concentrated on mixtures of ethoxylated compounds, while the fatigue testing looked at using phase-transformed materials^{11, 12} in combination with non-transformed compounds. Our starting formulation was a stripped-down version of one of the Air Force formulations and is given below:

COMPOUND	CONCENTRATION/2L
Triton X114 (@1,000ppm)	13.5 ml
Sodium Nitrate	7.0 gm
Sodium Nitrite	7.0 gm
Zinc Sulfate	1.0 gm

ELECTROCHEMICAL TESTS

The linear polarization program we purchased to do the inhibitor screening arrived with a major defect. As the time estimated for correcting the problem was 6 to 12 weeks, we decided to use the Stern-Geary polarization program which was supplied as part of the same operating system. The only limitation with using this particular program was that the operating algorithm for determining the data constants expected a non-linear response. (See pages 13-16 for further discussion of this problem.) The program for determining the pitting potential and pitting time was supplied by the same vendor who supplied the linear scan programs.

All the testing procedures used silver/silver chloride reference electrodes and platinum wire counter electrodes. The metal test electrodes were received with a 600 grit finish, which was removed using 400 grit silica carbide cloth, refinished to 600 grit, washed with deionized water, degreased using ethanol or an inhibited chlorinated solvent, blown dry, then immersed in the test solution. The tested surface of the metal electrode was removed using 120 grit silica carbide, then refinished using 240 grit and 600 grit cloths. Al 7075-T6 electrodes were used for all but the last month of electrochemical testing, when the supply ran low. T7351 electrodes were used in place of the T6 electrodes.

FATIGUE TESTS

All the fatigue tests were performed using a 30Hz crank and lever testing machine. Appendix C shows the three specimen configurations used for the fatigue tests in this program. The second configuration, vee-notched, exhibited the best sensitivity to changes in the test environment, had the

least data scatter, and was used for 95% of the tests. Appendix D shows the schematic of the fatigue test system. Al 7075-T7351 was used for 90% of the formulation screening so as to save the T6 coupons for the next test phase, because of the T6's extreme sensitivity to the surrounding environment. The T6 had to be used when the supply of -T7351 became very low, and there might not be enough to use in Phase IV of the program. The center-notched coupons were to be used in the last two phases of testing, primarily due to their longer fatigue lives in all environments tested.

The marine test solution was made using a commercial marine aquarium mix. The electrochemical test results using both the acidified and neutral solutions appeared to be very reproducible over the entire length of the test program, giving us a large measure of confidence in the consistency of the mixture.

RESULTS

The program tested in excess of 200 formulations, and 12 of these showed potential as general purpose corrosion inhibitors. In addition, six formulations increased the fatigue life of the test material in an aggressive environment. Some differences were found in the fatigue behavior between the T6 and T7351 when exposed to the same environment, which was not expected. We experienced some problems in reducing our electrochemical data which remain yet unresolved. We achieved our goal of producing four to eight candidate formulations as protection against environment assisted cracking, and in addition found those general corrosion formulations.

As discussed earlier, we had decided to have the test systems define our worst-case conditions, as ASTM type test solutions such as 3.5% sodium chloride are rarely encountered in actual outdoor exposures. Without performing a major study on the chemical nature of acid rain, we needed to find a good acid rain analog for our studies which both increased the general corrosion rate and decreased the fatigue life of the test metal.

We started the tests with the Al 7075-T6 electrochemical tests, proceeded to the T7351 electrochemical tests, and finished with the fatigue results. Not all the analogs were used in all the tests. The tests results of this portion of the testing are presented in Table 1.

The two things which stand out in the T6 results are the magnitude of the reduction in the fatigue life, and the lack of noticeable differences between the marine solution and the 3.5% sodium chloride test results. Closer inspection of these results shows that there is very little difference between the mist and the spray results.

The T7351 fatigue results appear to be totally the opposite of the T6 results. The marine solution produces the greater effect on the fatigue life of the metal. Also, there are observable effects due to pH and the test state. The Al 7075-T7351, while showing less reduction in the fatigue life effects, appears to be exhibiting an increased sensitivity to changes in the environment around it. Still, the

T7351's worst-case values are significantly better than the T6's best-case values in an aggressive environment.

A point of interest to note in the fatigue life data is that, except in one instance, the spray test environment data is higher than the mist test environment data. Due to the small difference in fatigue response of the T6, the T7351 was not tested using a neutral marine spray nor an acid marine mist test environment. The acid spray fatigue test using the 1:1 nitric-sulfuric analog was run to see if the extremely high apparent corrosion rate, 108 mils per year (mpy), would have any effect on the fatigue life of the T6.

The electrochemical results for both the T6 and the T7351 appear to have anomalous results when the marine solution is acidified using nitric acid. For the T6, there is a low apparent corrosion rate and high surface resistance coupled with a shift in the pitting potential and an increased initiation time. The T7351 results are just the opposite. In both cases, the results are not consistent with the balance of the test data in Table 1.

The analog we decided to use was the 9:1 (vol) sulfurous acid:nitric acid mixture. The basis of this decision was the increased general corrosion rate it induced in both the T6 and the T7351, and lack of change in the pitting initiation times. Ideally, we were looking for a reduction in the pit initiation time for both metals coupled with an increased general corrosion rate. This decision was made in accordance with the theories which linked environmentally assisted cracking susceptibility to pitting environments. Sulfuric acid was used for 204 of the 886 tests in place of the sulfurous acid.

Baseline Testing Results

The response of our test systems to known inhibitor formulations is presented in Table 2. The fatigue data shows the effectiveness of the Navy formulation using phase transformed materials. The particular Air Force formulation we chose to test appeared to be ineffectual in the mist environment, and possibly an aggressive agent itself, while the 1984 test results showed a positive effect on the T6 fatigue life in the spray environment when a neutral marine solution was used. In fact, this inhibitor solution, when dissolved in the acid marine solution, caused severe general corrosion of the aluminum parts of the fatigue tester. The resulting corrosion was heavier and faster than any other solution tested, including the uninhibited solutions.

A statistical comparison of the 1983 T6 control data with the Air Force and the Navy inhibitor results show that the Navy results are comparable to the T6 dry air test results, and the Air Force inhibitor did not decrease the T6 fatigue life. Table 3 summarizes the results of the statistical comparison. The difference in the 1983 and the 1984 fatigue results in control data are a result of using two different lots of metal and two different heats for each temper. The materials used in Fiscal Year (FY) 1983 were all consumed at that time and new materials were needed for FY 1984-1985.

AVERAGE—A17075-T7351

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Table 1. Solution Selection Test Results—Continued

METAL-MATRIX	FATIGUE LIFE 1,000 CYCLES	F _{CORR} vs. Ag/AgCl mVDC	AVERAGE—Al 7075-T6		PITTING POTENTIAL vs. SCE mVDC	INITIATION TIME PITTING SECONDS
			CORROSION RATE mpy (1)	SURFACE RESISTANCE Rp ohms (2)		
• Marine Solution	Mist 47/Spray 55	-747	1.08	2702	-647	155
Δ Acid Marine Solution/ Nitric Acid	Not Tested	-713	1.13	2600	-675	345
Δ Acid Marine Solution/ Sulfuric Acid	Not Tested	-720	36.1	88	-674	1,766
Δ Acid Marine Solution/ Sulfurous Acid	Not Tested	-705	58.3	54	-676	822
Δ Acid Marine Solution/ 9 vol. Nitric Acid; 1 vol. Sulfurous Acid	Not Tested	-719	39.7	74	-675	736
Δ Acid Marine Solution/ 1:1 vol. Nitric Acid; Sulfurous Acid	Not Tested	-720	59.3	51	-676	567
Δ Acid Marine Solution/ 1 vol. Nitric Acid; 9 vol. Sulfurous Acid	Mist 48/Spray 51	-720	58.3	54	-685	152
Δ Acid Marine Solution/ 1:1 vol. Nitric Acid; Sulfurous Acid	Spray 47	-724	108.0	28	-676	338
Δ Acid Marine Solution/ 1:1 vol. Sulfuric Acid; Sulfurous Acid	Not Tested	-738	64.0	47	Not Tested	
Δ Acid Marine Solution/ Phosphoric Acid	Not Tested	-731	63.7	47	Not Tested	
Δ Acid Marine Solution/ 1 vol. Nitric Acid; 9 vol. Sulfuric Acid	Not Tested	-719	63.0	48	-677	157
3.5% Sodium Chloride	Mist 40/Spray 34	-716	37.5	84	Not Tested	
Δ Acid 3.5% NaCl/Nitric Acid Dry Air	Mist 36/Spray 38 209	-720	35.9	84	Not Tested	

NOTES: (1) Calculated using fixed Tafel values.
(2) Average measured value.

Table 2. Baseline Test Results

INHIBITOR	FATIGUE LIFE 1,000 CYCLES	E _{CORR} vs. Ag/AgCl mVDC	AVERAGE—Al 7075-T6		SURFACE RESISTANCE Rp ohms (2)	PITTING POTENTIAL vs. SCE mVDC	INITIATION TIME PITTING SECONDS
			CORROSION RATE mpy (1)				
None : NMS : AMS	Mist 47 (7) Spray 51	-747 -720	1.08 58.3		2,702 54	-647 -685	155 152
β : NMS	Spray 59 (4,7)	-677	0.38		8,237	-690	660
β : AMS	Mist 37 (3) Spray 40 (4)	-724	12.00		242	-687	938
V : NMS	Not Tested	-722	15.00		217	Not Tested	
V : AMS		-702	24.00		139	-676	311
AlF #7 : NMS	Mist 46 (3,5,7) Spray 60 (3)	-707	14.97		219	-671	731
AlF #7 : AMS	Spray 44 (3)	-710	23.50		130	-674	565
Navy DNBDM : NMS	Mist 83 (4,5,6,7)	Not Tested				Not Tested	
Commercial 6, 7, 12 : NMS	Mist 54 (3,5,6,7)	Not Tested				Not Tested	
Cr (1%) ₃ Chromate : NMS : AMS	41 ₁ 38 ₁	-788 -784	0.19 0.23		15,987 12,715	Not Tested -624	137
Cr (1/2 %) Chromate : NMS : AMS		-718 -724	4.50 16.0		711 185	Not Tested Not Tested	

Table 2. Baseline Test Results—Continued

INHIBITOR	FATIGUE LIFE 1,000 CYCLES	E _{CORR} vs. Ag/AgCl mVDC	AVERAGE—AI 7075-T73		PITTING POTENTIAL vs. SCE mVDC	INITIATION TIME PITTING SECONDS
			CORROSION RATE mpy (1)	SURFACE RESISTANCE Rp ohms (2)		
None : NMS : AMS	Mist 63	-726	1.08	5,122	-627	182
	Spray 81	-714	70.5	74	-674	202
β : NMS	Not Tested	-682	0.18	31,000	-640	899
β : AMS	Not Tested	-693	3.10	1,874	-656	541
V : AMS	Not Tested	-681	10.0	599	-649	969
V : #9	Not Tested	Not Tested			-640	305
AF #7 : NMS	Not Tested	-691	26.5	235	-653	506
AF #7 : AMS	Not Tested	-696	14.5	384	-644	351

NOTES: (1) Calculated using fixed Tafel constants.

(2) Average value measured.

(3) Inhibitor in marine solution.

(4) Applied to surface of coupon before testing.

(5) Tests done in 1983, T6 Control = 50 KC fatigue life, dry air = 97 KC.

(6) Materials proved to be untestable using the linear polarization techniques available.

(7) Condensing humidity in test chamber resembling a very fine aerosol.

s = Solution concentration for electrochemical testing

t = Fatigue coupon dipped in full strength chromate conversion coating at room temperature

AMS = Acid marine solution, pH 3.50

NMS = Neutral marine solution, pH 6.97

β = Commercial inhibitor B

V = Commercial inhibitor V

AF#7 = Air Force Inhibitor Formula #7

Table 3. Comparison of Air Force and Navy Inhibitor Fatigue Data to Control Data

1983 DATA SETS	STATISTIC PROBABILITY	
	t *	f **
AF #7 and T6 Baseline Mist (Air Force)	18%	36%
AF #7 and T6 Dry Air	< 0.01%	< 0.01%
DNBN and T6 Dry Air (Navy)	3%	6%
DNBN and T6 Baseline Mist	<0.01%	<0.01%

* Analysis of variance; rejection limit probability $\leq 2.50\%$.

** Difference between 2 group means rejection limit probability $\leq 5.00\%$.

The results also showed that the inhibitors needed to be tested in both a spray and a mist environment. It is obvious that the worst-case test condition for the metal is not the same as that for an inhibitor. In the case of the Air Force formula tested, the primary reason for the difference is that the formulation was added to the basic test solution, rather than being applied to the surface of the fatigue coupon. At this time, we also established the minimum electrochemical criteria for any candidate formulation as < 8 mpy in the acid marine solution.

Electrochemical Screening Results

The original criterium of < 8 mpy for the polarization test results proved too high; in fact, there were 35 raw formulations having an indicated mpy < 1.00. All except one of these formulations contained both sodium molybdate and sodium hexametaphosphate. Two surfactants were found in 28 of the 35 formulations. These same two surfactants were also found in all 12 of the formulations with an mpy < 0.40. It was not possible to run fatigue life tests on all the formulations. Table 4 lists the 12 raw formulations having an indicated mpy < 0.40.

The mpy values are referred to as indicated due to a problem arising from the tafel generating algorithm expecting a non-linear response. Figure 1 shows the type of response the algorithm was designed to evaluate and Figure 2 shows the type of response our tests generated. The resulting problem is illustrated by Table 5. The beta values shift wildly for the same metal in the same test solution. After discussions with the vendor, we decided to use fixed beta values for evaluating all the screening results and also to rely on the changes in the Rp ohms to reflect the inhibitive powers of the formulations being tested. We continued to use the mpys calculated using the fixed beta values and the test Rp ohms as a matter of convenience as we were interested only in the relative changes.

**Table 4. General Corrosion Inhibitor Formulas
Raw Formulas**

TEST MATRIX	FORMULAS	E _{CORR}	R _p ohms*	mpy**	KC MIST
NMS		-726	5,122	1.08	63
AMS		-714	74	70.5	81
RCI-1	VN 430 H 100 2-Mercaptobenzothiazole (0.1%)	-711	134,690	0.04	55
RCI-2	VN 430 H 100 Dodecylbenzenesulfonic Acid Sodium Salt (0.1%)	-674	40,525	0.14	68
RCI-3	VN 430 H 100 Aminothiazole (0.1%)	-679	33,714	0.17	69
RCI-4	VN 430 H 100 TFA-8	-667	29,235	0.22	63
RCI-5	VN 430 H 100 MO 6	-662	29,038	0.22	61
RCI-6	VN 430 H 100 Standapol (0.5%)			0.23	69
RCI-7	VN 430 H 100 Sulfosuccinic Acid	-671	26,446	0.25	Not Tested
RCI-8	VN 430 H 100 ML5 MO 6	-681	23,301	0.25	70
RCI-9	VN 430 H 100 ML 5 MO 6 P31R1 R (0.1%)	-701	21,869	0.28	Not Tested
RCI-10	VN 430 H 100 Petrowet R (0.1%)	-682	19,517	0.29	56
RCI-11	ML 5 MO 6 H 100	-685	21,244	0.30	79
RCI-12	VN 430*** H 100 Dodecylbenzenesulfonic Acid (0.5%)	-666	15,471	0.38	****

NOTE: See Appendix E for list of test chemicals.

* Measured

** Using constant Beta values.

*** All formulas contained sodium molybdate and sodium hexametaphosphate.

**** Bad data point ; fatigue machine broken.

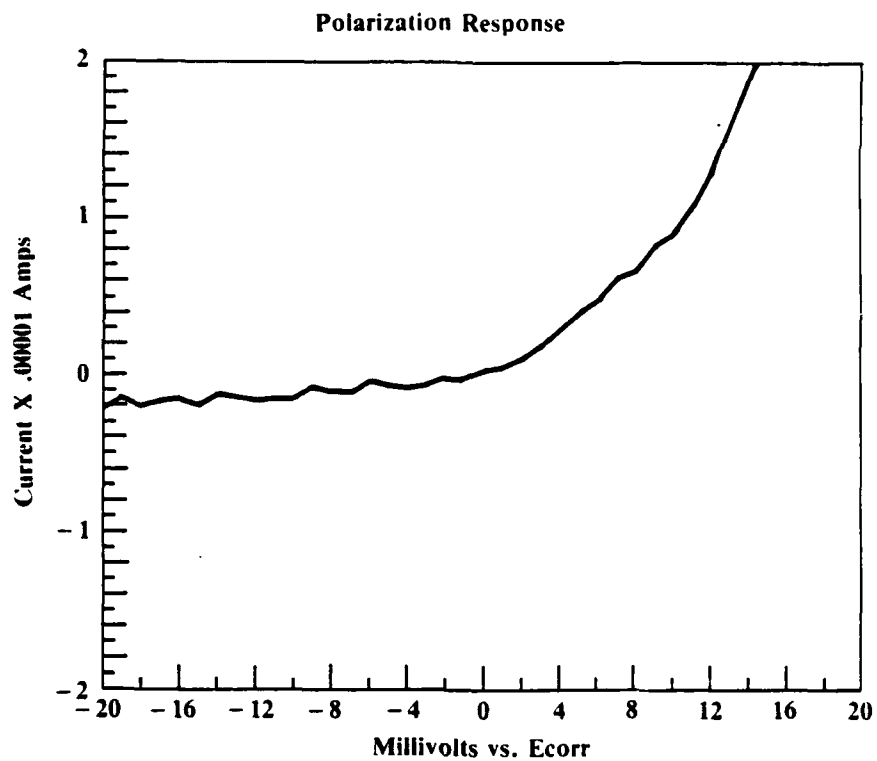


Figure 1. Form of Response Expected by Tafel Algorithm

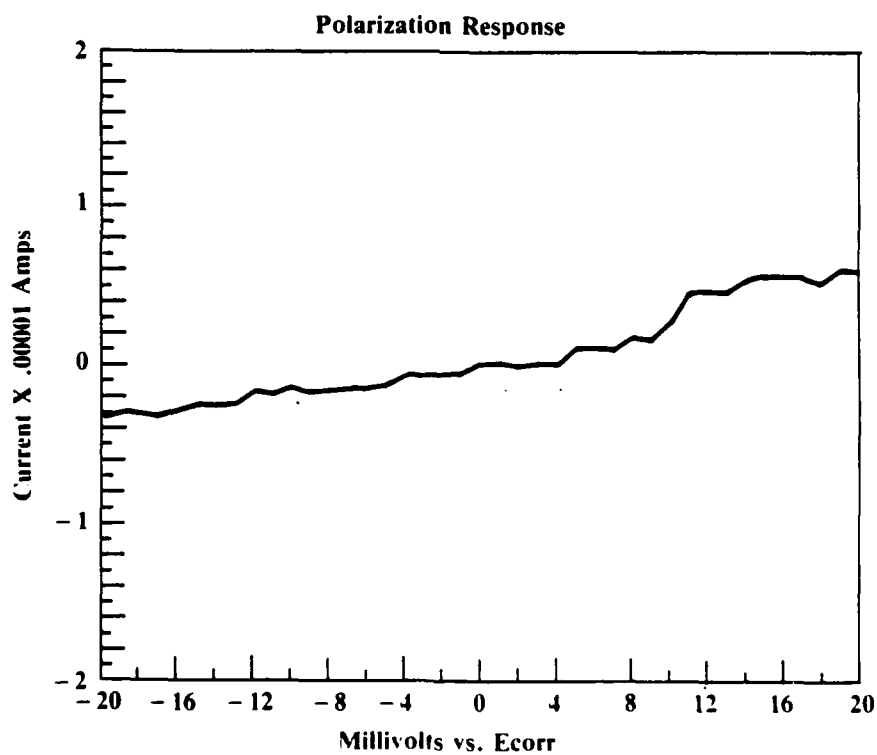


Figure 2. Form of Actual Response

**Table 5. A Sample of Data Scatter for the Polarization Tests
7075-T6 in Neutral Marine Solution**

ELECTRODE	Rp ohms	mpy	β	β
IV	860	1.40	56	7
III	3,200	0.31	18	8
VI	3,600	0.86	39	28
I	1,700	0.81	444	8
V	3,400	1.20	50	37
VII	3,000	1.10	35	36
V	2,100	1.00	27	19
AVG	2,551	0.95	95.6	20.4
STD DEV	1,019	0.35	154.2	13.3

The constant beta values used were derived using T6 weight loss values and the average Rp ohms values measured. The T6 weight loss source is Godard,⁶⁰ the 5-year exposure results at Harbor Island, NC. The average Rp ohm values used are for the neutral marine solution, given in Table 2. The T6 corrosion rate was used to derive both the T6 and the T7351 beta constants. At this point in the program, the actual rates were not critical. The derived values for the tafel constants were:

$$\begin{aligned} \text{T6 } \beta_{(a, c)} &= 25.627 \\ \text{T73 } \beta_{(a, c)} &= 48.587 \end{aligned}$$

Fatigue Screening Results

The results from the fatigue life tests show that there were six raw formulations which had a positive effect on the fatigue life of the metal tested. The effectiveness of each formulation changed with the type of test environment. Two formulations showed a greater degree of environmentally assisted cracking inhibition in the mist environment, while the other four were more effective when in a spray environment. Five of the six formulations used phased transformed materials. The sixth formula is also contained in Table 4, which listed the 12 best general corrosion inhibitors. Table 6 lists the six environmentally assisted cracking formulations and test results.

The 12 general inhibitor formulas and the six environmentally assisted cracking inhibitor formulas are considered to be raw formulations. This is because no effort was made to maximize their inhibiting effects by adjusting the concentration of the individual components.

Table 6. Candidate EAC Inhibitor Formulas

INHIBITORS USED	ENVIRONMENT	FATIGUE LIFE KC	E _{CORR} vs. Ag/AgCl	R _p ohms	mpy
None - NMS	Mist	63	-726	5,122	1.08
None - AMS			-714	74	70.5
A 336 - AMS	Mist	61	Not Tested		
CA, PA 336 - AMS	Mist	88	-709	2,409	2.3
A 336, PA 336 - AMS	Mist	85	Not Tested		
CE 32, PA 336 - AMS	Mist	91	-700	1,227	4.98
HD 100, PA 336 - AMS	Mist	105	-693	2,770	2.02
PA 336 - AMS	Mist	84	-694	3,929	1.10
H 100, MO-6, ML-5	Mist	79	-701	21,868	0.28

NMS = Neutral marine solution

AMS = Acid marine solution

CA = Cellosolve acetate

A 336 = Aliquat 336

PA 336 = Phase transformed 336 solution containing sodium molybdate and sodium phosphate

CE = Cellosolve

The big problem we had to overcome was getting any inhibitor formula to adhere to the surface oxide of the aluminum alloy. In order to address this problem, we looked at the effects of surface preparation prior to applying an inhibitor, and the use of wetting agents. The results of these tests are given in Tables 7 and 8.

SECTION III. CONCLUSION

At the close of the program, we achieved those goals which had been set for this phase of the program—the identification of six to eight candidate environmentally assisted cracking inhibitor formulations. Additionally, we found 12 candidates that could be used as general corrosion inhibitors.

Table 7. Effects of Surface Pretreatment

TREATMENT/INHIBITOR	K CYCLES	
	MIST	SPRAY
T6	47	51
T6	Chromate	38
	Cr/B (spray)	41
	Cr/B (dipped)	42
	B (dipped)	30
	Cr/Latex Binder	45
	Latex Binder	62
T73	T73	81
	Bright Dip	85
	BD/W912 (1/2 %)	90
	BD/W912 (1/2 %) + Tolyltriazole	96
	BD/Cr/ W912 (1/2 %)	71
	BD/Cr/ W912 (1/2 %) + Tolyltriazole	55
	Cr/ W912 (1/2 %)	56
	Cr/ W912 (1/2 %) + Tolyltriazole	78
	W912 (1/2 %)	77
	W912 (1%), Triton x-114	68
	W912 (1/2 %) + Triton x 114	70
	Phytic Acid, Molybdic Acid, Tolyltriazole, W912 (1/2 %), No MO ₄ and PO ₄	67
	Phytic Acid, Molybdic Acid, Tolyltriazole, W912 (1/2 %), No MO ₄ and PO ₄ + Triton x 114	72
	Hot Phytic Acid	49
	HPA/ W912 (1/2 %) + Triton x 114	35
	HPA/W912 (1%), Triton x -114	92
	HPA/Cr/W912 (1%), Triton x -114	102
	HPA/CF-32, Hydrazine Sulfate	108
	HPA/W912 (1/2 %) + Triton x 114 without Hexametaphosphate	46

NOTES: All formulas contain both sodium hexametaphosphate and sodium molybdate unless noted otherwise.

See Appendix E for list of test chemicals.

Cr = Chromate conversion coating

B = Commercial inhibitor B

HPA = Hot Phytic Acid

Table 8. Wetting Agents

BASE SOLUTION: TRITON CF-32 AND HYDRAZINE SULFATE

AGENT	K CYCLES	FILM THICKNESS (MICRONS)
Pluronic 31R1	65	4
Tetronic 1501	64	4
Tetronic 901	63	5
Tetronic 1102	58	4
Imboil PDA	65	5
Monawet MO-70	61	3
Monafax 785	64	2
Neodol 91-6	67	4
Neodol 25-3A	60	3
Neodol 91-8	53	3
Petrowet "R"	55	3
Olin SL-42	64	3
Olin S-405LF	56	3
Olin S-505LF	61	4
Mazawet SD	63	4
Neodol 25-3S	62	3
HP/base solution	108	7
HP/base/mist	141	6
AC/base	56	—

NOTE: See Appendix E for list of test chemicals.

HP = Hot phytic acid pretreatment

AC = Pretreatment using an aluminum cleaning solution

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APPENDIX A. ELECTROCHEMICAL TEST OUTLINE

Baseline

Marine Mix
Acid Mixtures



Linear Polarization Potential (Linpol)
Galvanic Pitting Potential (Galpit)



Commercial Formulations (Marine Mix/Acidified Marine Mix)

Boeshield
AF #7
VCI 425



Linpol & Galpit



Original Formulations (Acidified Marine Mix)

Molybdates/Hexametaphosphates
Inorganic Additions
Organic Additions/Substitutes



Linpol Screening



Original Formulation (mpy < 8.00)

Fatigue Testing



Full Series Testing

3.5% NaCl
3.5% NaCl @ pH 3.5
Marine Mix @ pH 8.0



Linpol
Galpit

Marine Mix @ pH 3.5



Galpit only

Rerun Best of Formulations using tap & river water as solution solvent
(Reruns series at 30°F solution temperature)

APPENDIX B. FATIGUE TEST OUTLINE

BASELINE TESTING

Dry (RH 36%) Humid (RH 85-90%) Acid Humid (RH 85-90% & pH 3.5) Spray (RH 90-100%) Acid Spray (RH 90-100%)]	3.5% NaCl Marine Mix]	Relief Notched 6061-T6
---	---	-------------------------	---	---------------------------

Dry Humid Acid Humid Spray Acid Spray]	Marine Mix]	Vee Notched 7075-T6
---	---	------------	---	------------------------

Dry Humid Acid Spray]	Marine Mix]	Center Notched 7075-T6 (7075-T73 Vee & Center)
----------------------------	---	------------	---	--

EVALUATION

Latex Binder Material

Humid Acid Spray]	Marine Mix]	Vee Notched 7075-T6
---------------------	---	------------	---	------------------------

Use Alodine 1200 (alone)

Humid Acid Spray]	Marine Mix]	Vee Notched 7075-T6
---------------------	---	------------	---	------------------------

Use Alodine 1200 & Latex Binder

Humid
Acid Spray

☐

Marine Mix

☐

Vee Notched
7075-T6



EVALUATION OF ORIGINAL FORMULATIONS
(mpy < 8.00 Linpol)

Humid
Acid Spray

☐

Marine Mix

☐

Vee Notched
7075-T6



Humid
Acid Spray

☐

3.5% NaCl

☐

Vee Notched
7075-T6



Humid
Acid Spray

☐

Marine Mix
3.5% NaCl

☐

Center Notched
7075-T6



Humid
Acid Spray

☐

Marine Mix
3.5% NaCl

☐

Center Notched
7075-T6



Humid
Acid Spray

☐

Marine Mix
3.5% NaCl

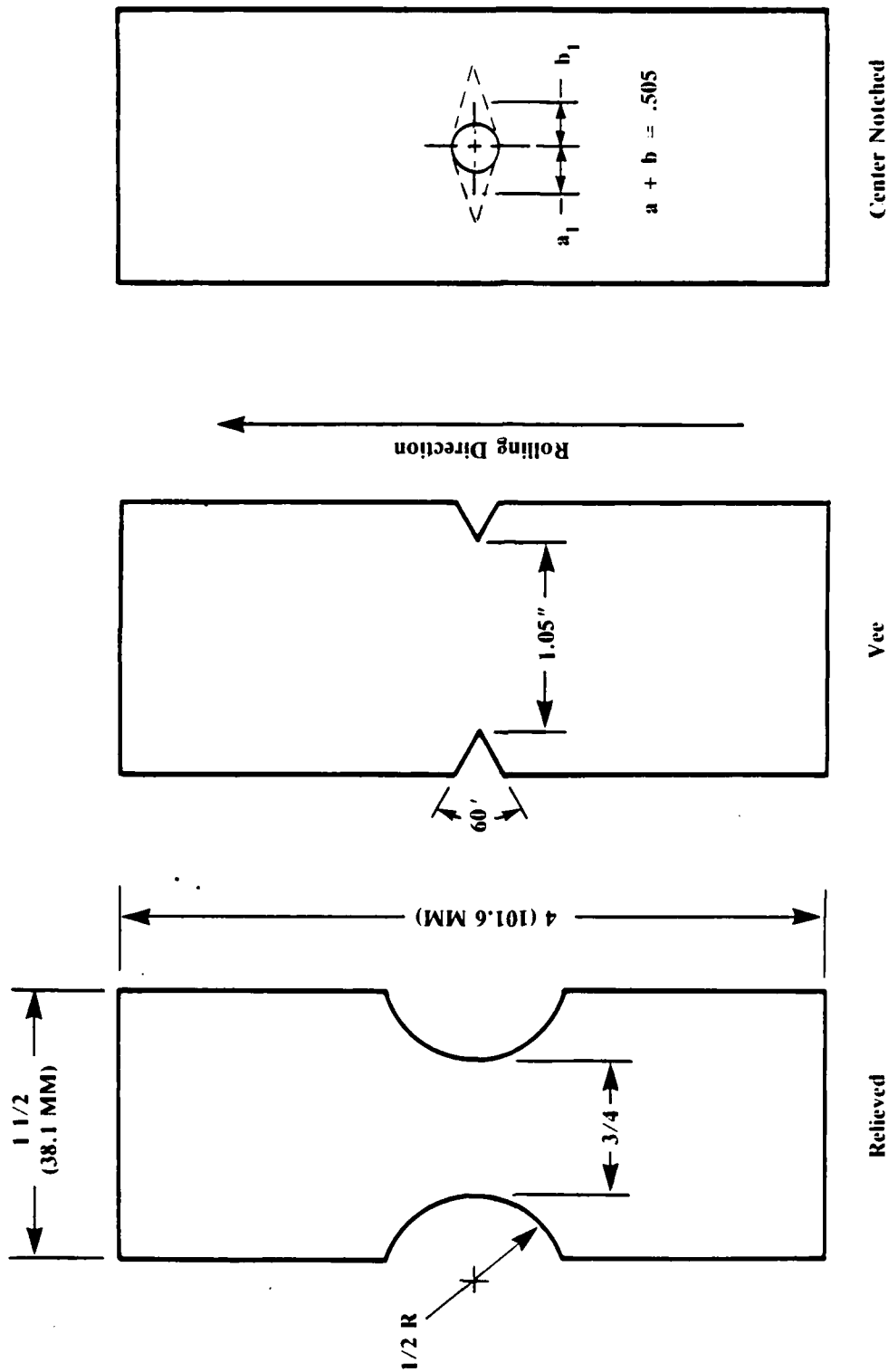
☐

Vee & Center
7075-T73

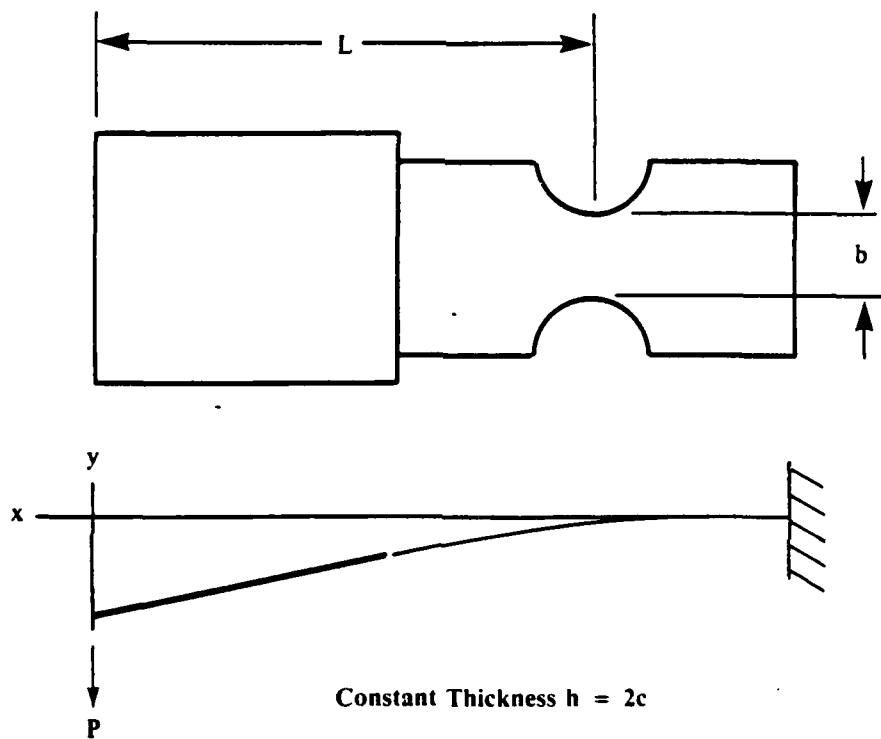
Best of Formulations - Retest

- Using tap and river water as solution solvent
- Best of combined results
- Static crack growth rates

APPENDIX C FATIGUE COUPONS



Bending Specimen-Fixed Cantilever Constant Amplitude of Force



Specimen #3
Short Arm

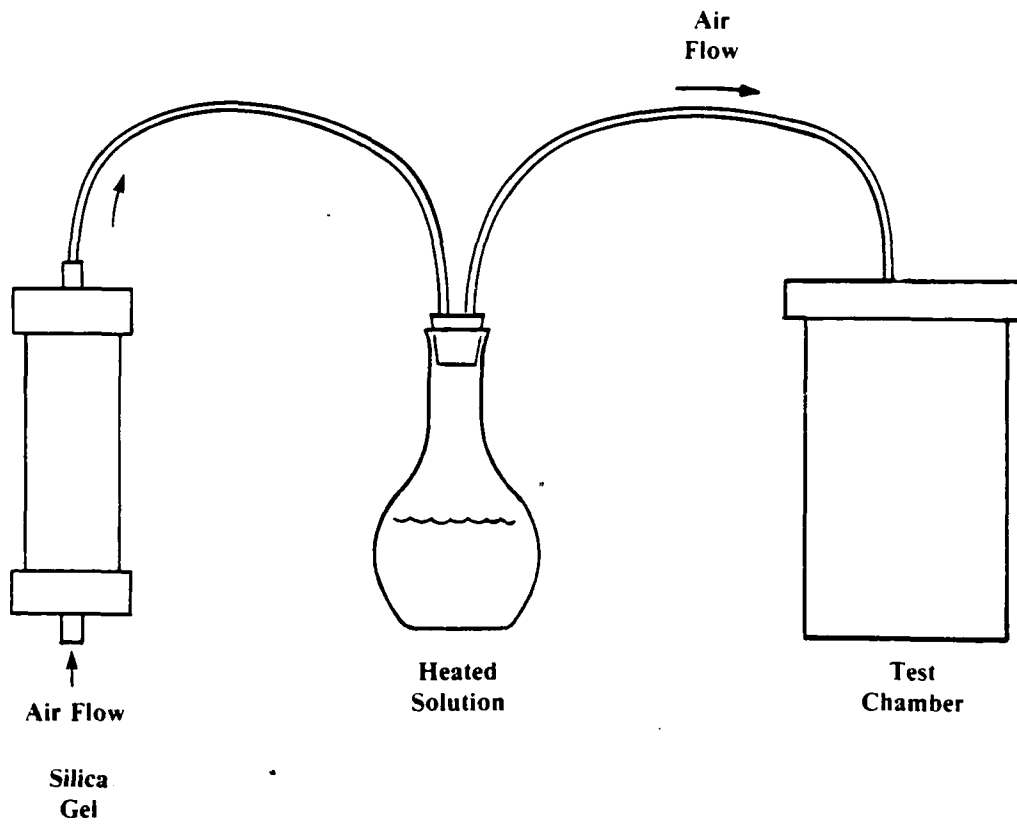
$$b = 3/4$$

$$L = 4-3/4$$

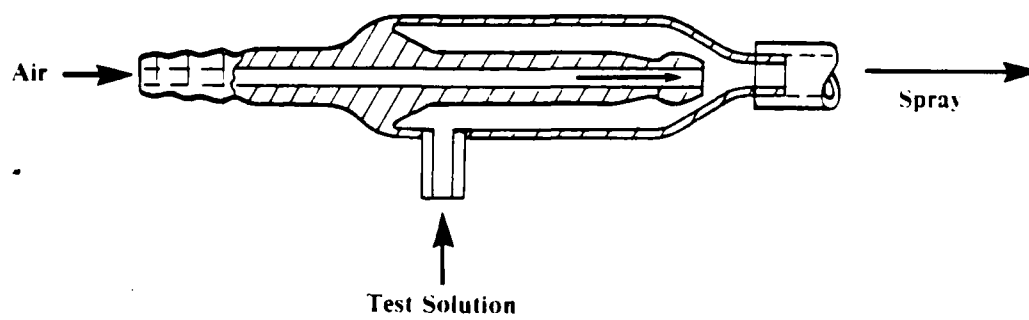
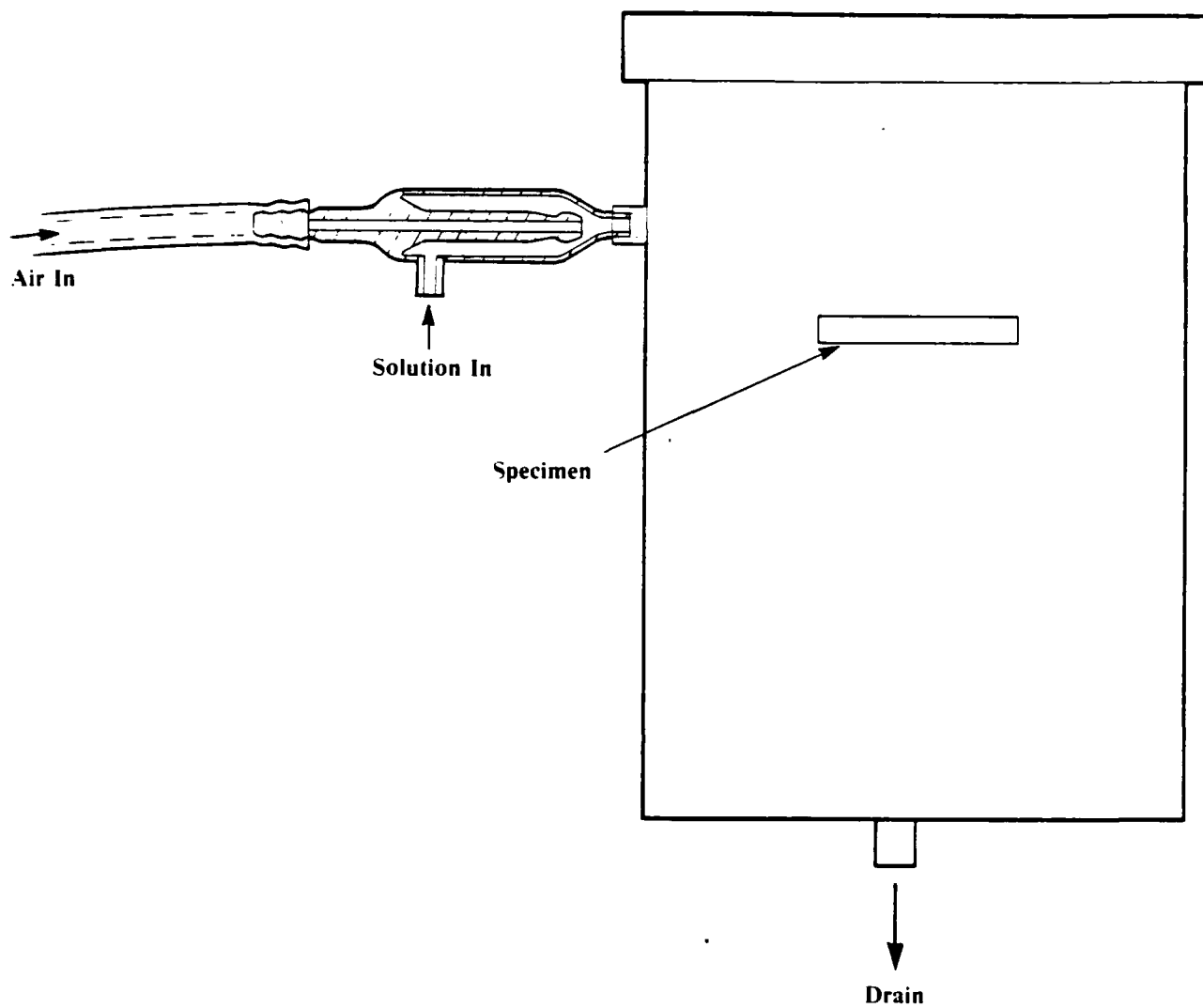
$$S = 38P/h^2$$

Critical Dimensions for Load Calculations

APPENDIX D FATIGUE TEST SYSTEM SCHEMATIC



Schematic of Mist Test System



Spray Test Set Up

APPENDIX E

LIST OF TEST CHEMICALS

PRODUCT	CHEMICAL NAME
Petrowet "R"	Sodium Alkyl Sulfonate
Stepantan H-100	Branched Dodecylbenzene Sulfonic Acid
Witco 912	Sulfonated Salts of Fatty Acids Ethoxylate
Emulphor VN-430	Polyethoxylated Oleyamine
Industrol TFA-8	Fatty Acid
Quadrol	N, N, N', N' (2-Hydroxylpropyl) Ethylene Diamine
Triton CF-32	Amine Polyglycol Condensate
Industrol MO-6	6 mole Ethylene Oxide
Industrol ML-5	5 mole Ethylene Oxide Adduct of Lauric Fatty Acid
Triton X-114	Ethyleneoxide-Octoxphenoxy-Polyethoxyethanol
Aliquat 336	Tricaprylyl Methyl Ammonium Chloride
Biosoft HD-100	Anionic/Non-Anionic Blend
Monafax 785	Phosphate Ester
Monawet MO-70	Diocetyl Sodium Sulfosuccinate
Olin SL-42	Linear Alcohol
Olin S-405LF	Linear Alcohol
Olin S-505LF	Linear Alcohol
Pluronic 31R1	Propyl Ethyl Polymer
Tetronic 901	Amine
Tetronic 1102	Amine
Tetronic 1501	Amine
Neodol 25-3A	Ammonium Ethoxysulfate Salt
Neodol 25-38	Sodium Ethoxysulfate Salt
Neodol 91-6	Alcohol Ethoxylate
Neodol 91-8	Alcohol Ethoxylate
Indoil PDA	Phosphate Ester
Phytic Acid	Inositolhexaphosphoric Acid

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